CHAPTER II

EXPERIMENTAL

2.1 Chemicals

Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck Kieselgel 60 F_{254}) (Merck KgaA, Darmstadt, Germany). Column chromatography was performed using silica gel 0.06-0.2 mm or 70-230 mesh ASTM (Merck Kieselgel 60 G, Merck KgaA, Darmstadt, Germany). Solvents used in synthesis were reagent or analytical grades. Solvent used in column chromatography were distilled from commercial grade. Other reagents were purchased from the following venders:

- Labscan (Bangkok, Thailand): chloroform, dichloromethane, concentrated hydrochloric acid, toluene, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), acetonitrile, acetone, *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), acetic acid

- Acrös Organic (USA): quinoline, 2,3-dichloroquinoxaline, sodium hydride

- Carlo Erba Reagent (Milan, Italy): potassium carbonate (K_2CO_3), sodium sulfide nonahydrate ($Na_2S.9H_2O$), pyridine, dichloromethane

- Fluka Chemical Company (Buchs, Switzerland): sodium metal (Na), cuprous oxide (Cu_2O), 4-(dimethylamino)pyridine (DMAP), triethylamine

- Merck Co. Ltd. (Darmstadt, Germany): diethyl ether (Et_2O), sodium hydroxide (NaOH), anhydrous sodium sulfate (Na_2SO_4), chloroacetyl chloride, ethanol absolute

- Riedelde Haën: anhydrous iron (III) chloride ($FeCl_3$), triethylamine

- Aldrich : ethyl chloroacetate, diethyl oxalate, *trans*-1,4-dibromo-2-butene, *N*-bromosuccinimide (NBS), 3,4-dichloro-1,2,5-thiadiazole, sodium hydride, pyridinium tribromind, sodium sulfite

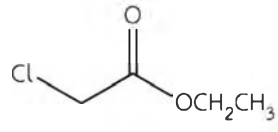
- Panreac : anhydrous magnesium sulfate ($MgSO_4$)
- Ajax Finechem Pty Ltd : calcium chloride
- Cambridge Isotope Laboratories Inc., USA : deuterated chloroform, deuterated dimethylsulfoxide, deuterated acetone

2.2 Instruments and equipments

Melting points were determined with a Stuart Scientific Melting Point SMP1 (Bibby Sterlin Ltd., Staffordshire, UK). ^1H NMR and ^{13}C NMR spectra were obtained from Varian Mercury NMR spectrometer operated at 400.00 MHz for ^1H and 100.00 MHz for ^{13}C nuclei (Varian Company, USA) using deuterated chloroform ($CDCl_3$), deuterated dimethylsulfoxide (DMSO-d_6) or deuterated acetone (Acetone-d_6) as the solvent and tetramethylsilane as the internal standard relative to which the chemical shifts (δ) are given. IR spectra of all monomers and polymer solid samples were analyzed as neat and recorded on a Nicolet 6700 FT-IR RXI spectrometer. Mass spectra were recorded on Water Micromass Quatto micro API ESCi (Waters, USA). All samples were dissolved in acetronitrile, ethyl acetate, methanol or acetone. UV-Vis absorption spectra were recorded on UV-VISIBLE Spectrometer: UV-2550 (Shimadzu Corporation, Kyoto, Japan).

2.3 Monomer synthesis

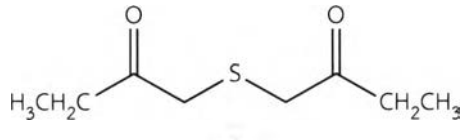
2.3.1 Ethyl chloroacetate 1



1

Chloroacetyl chloride (50 mL, 500.00 mmol) was added dropwise to ethanol (32 mL, 550.00 mmol) at 0 °C for 30 min. The reaction mixture was allowed to mix and stir for 3 h under nitrogen atmosphere. The reaction mixture was then warmed to room temperature. The mixture was quenched with 2 M sodium hydroxide and extracted with diethyl ether. The organic layer was dried with anhydrous sodium sulfate, filtered and distilled under reduced pressure to yield the product as colorless liquid. (55 mL, 99.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.21 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 2H), 1.23 (t, *J* = 7.2 Hz, 3H) **(Figure A.1, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.5, 62.2, 40.3, 14.1 **(Figure A.2, Appendix A)**. IR (ATR, cm^{-1}): 2968 (-CH st), 1725 (C=O st) **(Figure A.3, Appendix A)**.

2.3.2 Diethyl thiodiglycolate 2

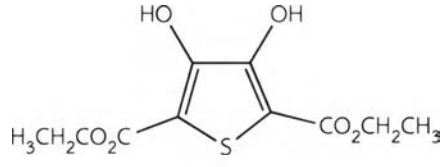


2

An addition funnel containing sodium sulfide nonahydrate ($Na_2S.9H_2O$, 12.000 g, 50.00 mmol) in water (30 mL) was added dropwise over period of 30 min. to the solution of compound **1** (13.200 g, 55.00 mmol) in acetone (50 mL), stirring at 60 °C under nitrogen atmosphere. The reaction mixture was then stirred for additional 2.5 h at reflux under nitrogen atmosphere and then cooled to room temperature and added water (20 mL). It was extracted with ethyl acetate, dried over anhydrous magnesium

sulfate, filtered and distilled under reduced pressure to give the compound as pale yellow liquid. (5.000 g, 49.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.20 (q, *J* = 7.1 Hz, 4H), 3.39 (s, 4H), 1.30 (t, *J* = 7.0 Hz, 6H) **(Figure A.4, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.5, 61.1, 33.3, 13.9 **(Figure A.5, Appendix A)**. IR (ATR, cm^{-1}): 2980, 2936 (-CH st), 1790 (C=O st) **(Figure A.6, Appendix A)**. MS: $[M+Na]^-$ m/z = 229.05 **(Figure A.7, Appendix A)** [46].

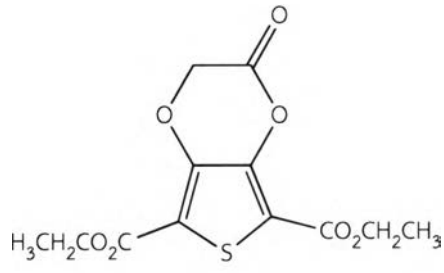
2.3.3 Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate 3



3

Sodium metal (2.400 g, 100.00 mmol) in ethanol (75 mL) was stirred in ice bath for 1 h. Compound **2** (2.000 g, 9.00 mmol) and diethyl oxalate (4.500 g, 14.00 mmol) in ethanol (75 mL) were added dropwise over a period of 30 min under nitrogen atmosphere in ice bath. The reaction mixture was stirred for 2.50 h at reflux under nitrogen atmosphere. It was then cooled to room temperature and added water (300 mL) and acidified with concentrated hydrochloric acid. The precipitated solid was filtered to afford the product as a pale yellow powder. (1.470 g, 63.0%). mp. 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.37 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 4H), 1.39 (t, *J* = 7.1 Hz, 6H) **(Figure A.8, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.5, 151.6, 107.1, 61.7, 14.0 **(Figure A.9, Appendix A)**. IR (ATR, cm^{-1}): 3293 (-OH st), 2987 (-CH st), 1661 (C=O st), 1508 (C=C st) **(Figure A.10, Appendix A)**. MS: $[M+H]^+$ m/z = 259.20 **(Figure A.11, Appendix A)** [47].

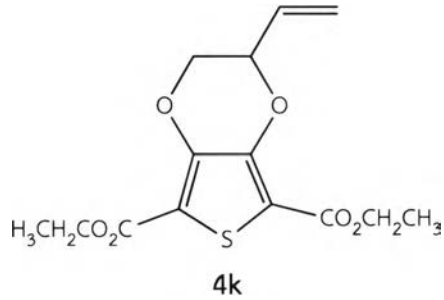
2.3.4 Diethyl 2-oxo-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5,7-dicarboxylate 4j



4j

Compound **3** (0.520 g, 2.00 mmol), chloroacetyl chloride (0.16 mL, 2.00 mmol), triethylamine (0.69 mL, 5.00 mmol) in dichloromethane (10 mL) were allowed to mix and stir at room temperature for 4 h under nitrogen atmosphere. The reaction mixture was evaporated and purified by column chromatography using hexane/ethyl acetate (1 : 1) as eluent to give the product as a white power (0.050 g, 16.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.30 (s, 2H), 4.29 – 4.19 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 6H) **(Figure A.12, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.8, 164.0, 163.4, 158.2, 152.6, 136.3, 122.2, 105.6, 60.6, 60.2, 38.8, 38.6 **(Figure A.13, Appendix A)**. IR (ATR, cm^{-1}): 2985 (-CH st), 1675, 1713 (C=O st), 1495 (C=C st), 1303 (C(O)-O st) **(Figure A.14, Appendix A)**. MS: $[M+Na]^+$ m/z = 324.09 **(Figure A.15, Appendix A)**.

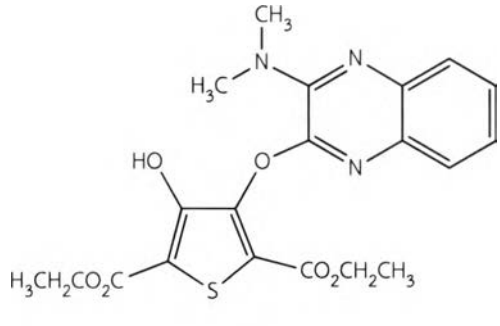
2.3.5 Diethyl 2-vinyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5,7-dicarboxylate 4k



4k

Compound **3** (0.260 g, 1.00 mmol), trans-1,4-dibromo-2-butene (0.320 g, 1.50 mmol), 4-dimethylaminopyridine (0.012 g, 0.10 mmol) and potassium carbonate (0.414 g, 3.00 mol) in dimethylformamide (10 mL) were allowed to mix and stir for 1 h at reflux under nitrogen atmosphere. The mixture was then cooled to 0-5 °C and added cold water (20 mL). The mixture was extracted with ethyl acetate and washed with 1 M sodium hydroxide and water. The organic layer was dried over anhydrous magnesium sulfate, filtered and distilled under reduced pressure. The product was purified by column chromatography using hexane/ethyl acetate (4:1) as eluent to yield the product as white needle crystal (0.166 g, 53.2%). mp. 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.87 (m, 1H), 5.54 (d, *J* = 17.3 Hz, 1H), 5.39 (d, *J* = 10.7 Hz, 1H), 4.76 (m, 1H), 4.37 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 4H), 4.04 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 6H) **(Figure A.16, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.7, 144.7, 144.6, 130.5, 120.4, 111.8, 111.6, 74.2, 67.8, 61.3, 61.2, 14.2 **(Figure A.17, Appendix A)**. IR (ATR, cm^{-1}): 2983 (-CH st), 1702 (C=O st), 1502, 1453 (C=C st), 1268 (C(O)-O st) (**Figure A.18, Appendix A**). MS: $[M+Na]^+$ m/z = 335.27 **(Figure A.19, Appendix A).**

2.3.6 Diethyl 3-((3-(dimethylamino)quinoxalin-2-yl)oxy)-4-hydroxy-thiophene-2,5-dicarboxylate 4l

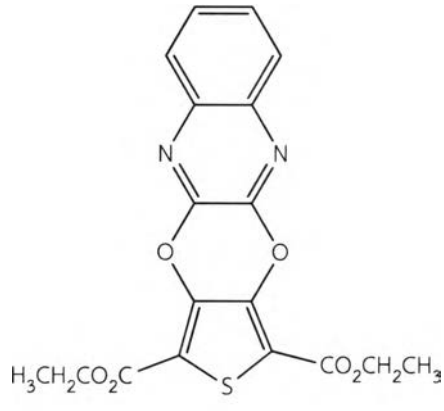


4l

Compound **3** (0.260 g, 1.00 mmol), 2,3-dichloroquinoxaline (0.218 g, 1.10 mmol), sodium hydride (0.120 g, 5.00 mmol) in 9 : 1 solvent mixture of tetrahydrofuran (9 mL) and dimethylformamide (1 mL) were mixed and allowed to stir at room temperature for 90 h and at reflux for 49 h under nitrogen atmosphere. The mixture

was then cooled to room temperature and quenched with water, extracted with ethyl acetate and washed with 1 M sodium hydroxide and water. The organic layer was dried over anhydrous sodium sulfate, filtered and distilled under reduced pressure. The compound was purified by column chromatography using hexane/ethyl acetate/acetic acid (9 : 0.9 : 0.1) as eluent, affording a white power (0.043 g, 10.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (d, *J* = 8.2 Hz, 1H), 7.49 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.43 (dd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 7.30 – 7.24 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.23 – 4.15 (m, 2H), 3.37 (s, 6H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H) **(Figure A.20, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.4, 160.2, 155.4, 148.3, 146.6, 140.6, 139.5, 127.5, 126.5, 125.5, 124.8, 106.9, 61.8, 61.6, 40.6, 14.2, 13.8. **(Figure A.21, Appendix A)**. $[M+H]^+$ m/z = 409.31 **(Figure A.22, Appendix A)**.

2.3.7 Diethyl thieno[3',4':5,6][1,4]dioxino[2,3-*b*]quinoxaline-1,3-dicarboxylate 4m

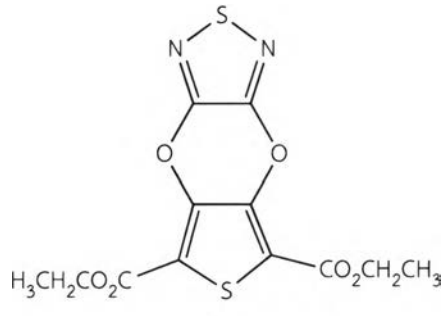


4m

Compound **3** (0.260 g, 1.00 mmol), 2,3-dichloroquinoxaline (0.049 g, 0.25 mmol), sodium hydride (0.060 g, 2.50 mmol), 8 mL of *N*-methyl-2-pyrolidone were allowed to mix and stir for 3 h at reflux under nitrogen atmosphere. The reaction mixture was then cooled to 0 °C and quenched with cool water, extracted with ethyl acetate and washed with 1 M sodium hydroxide and water. The organic layer was dried over anhydrous magnesium sulfate, filtered and distilled under reduced pressure. The crude was purified by column chromatography using hexane/ethyl acetate (4 : 1) as

eluent to obtain the product as a pale yellow powder (0.059 g, 61.2%). mp. 189 °C (dec.) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.92 (dt, *J* = 6.8, 3.4 Hz, 2H), 7.68 (dd, *J* = 6.3, 3.4 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 4H), 1.44 (t, *J* = 7.1 Hz, 6H) **(Figure A.23, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 141.7, 139.0, 129.7, 127.6, 115.0, 115.0, 62.1, 14.2 **(Figure A.24, Appendix A)**. IR (ATR, cm^{-1}): 2992 (-CH st), 1718 (C=O st), 1514, 1417 (C=C st), 1366, 1327 (C-N st), 1267 (C(O)-O st) **(Figure A.25, Appendix A)**. $[M+H]^+$ m/z = 386.98 **(Figure A.26, Appendix A)**.

2.3.8 Diethyl thieno [3',4':5,6] [1,4] dioxino [2,3-*c*] [1,2,5]thiadiazole-5, 7-dicarboxylate 4n

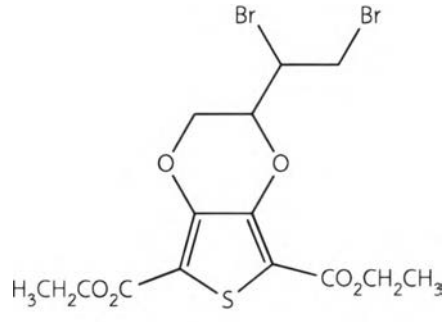


4n

Compound **3** (0.260 g, 1.00 mol), 3,4-dichloro-1,2,5-thiodiazole (0.02 mL, 0.25 mmol), potassium carbonate (0.518 g, 2.50 mmol), 8 mL of dimethylsulfoxide were mixed and allowed to stir for 6 h at reflux under nitrogen atmosphere. The reaction mixture was then cooled to 0 °C and quenched with cool water. The reaction mixture was extracted with ethyl acetate and washed with 1 M sodium hydroxide and water. The organic layer was dried over anhydrous magnesium sulfate, filtered and distilled under reduced pressure. The product was purified by column chromatography using hexane/ethyl acetate (9 : 1) as eluent to afford an orange powder (0.016 g, 9.4%). mp. 135-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.42 (q, *J* = 7.1 Hz, 4H), 1.41 (t, *J* = 7.1 Hz, 6H) **(Figure A.27, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 159.2, 144.6, 139.3, 115.2, 62.2, 14.1 **(Figure A.28, Appendix A)**. IR (ATR, cm^{-1}): 2974 (-CH st), 1710

(C=O st), 1256 (C(O)-O st) **(Figure A.29, Appendix A).** $[M+H]^+$ m/z = 342.96 **(Figure A.30, Appendix A)**.

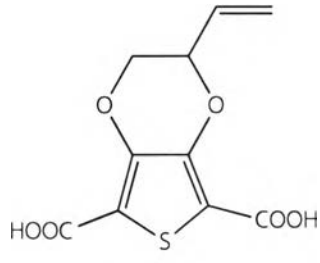
2.3.9 Diethyl 2-(1,2-dibromoethyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5,7-dicarboxylate 4p



4p

Compound **4k** (0.312 g, 1.00 mmol), pyridinium tribromind (0.959 g, 3.00 mmol), pyridine (0.40 mL, 5.00 mmol) in acetronitrile (8 mL) were allowed to mix and stir for 3 h at reflux under ambient atmosphere. The reaction mixture was then cooled to room temperature and quenched with 1 M sodium sulfite and washed with 10% hydrochloric acid, water and saturated sodium chloride. The product was purified by column chromatography using hexane/ethylacetate (1 : 1) as eluent to give a product as yellow oil (0.420 g, 89.4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.70 (dt, *J* = 8.8, 2.2 Hz, 1H), 4.66 – 4.60 (m, 1H), 4.52 – 4.44 (m, 1H), 4.41 – 4.28 (m, 4H), 4.15 (t, *J* = 10.4 Hz, 1H), 4.07 (dd, *J* = 11.5, 4.8 Hz, 1H), 3.93 – 3.83 (m, 1H), 1.37 (q, *J* = 7.0 Hz, 6H). **(Figure A.31, Appendix A)** ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.6, 144.3, 112.7, 73.9, 70.9, 68.4, 66.0, 61.3, 46.9, 34.1, 30.5, 14.2 **(Figure A.32, Appendix A)** IR (ATR, cm^{-1}): 2982 (-CH st), 1694 (C=O st), 1508 (C=C st), 1264 (C(O)-O st) **(Figure A.33, Appendix A)**

2.3.10 2-Vinyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5,7-dicarboxylic acid 5k



5k

Compound **4k** (0.312 g, 1.00 mmol), 10 mL of 1 M sodium hydroxide, 1 mL of ethanol were mixed and allowed to stir for 2 h at reflux under nitrogen atmosphere. The mixture was then cooled to room temperature and washed with ethyl acetate (10 mL). The separated aqueous layer was added concentrate hydrochloric acid (5 mL) to afford a pale yellow powder after filtration. (0.237 g, 92.5%). mp. 200 °C (dec.) ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 5.91 (m, 1H), 5.48 (d, *J* = 17.3 Hz, 1H), 5.31 (d, *J* = 10.7 Hz, 1H), 4.80 (m, 1H), 4.38 (m, 1H), 4.04 (m, 1H) **(Figure A.34, Appendix A)**. ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 161.1, 144.5, 144.0, 132.4, 122.4, 119.4, 112.8, 74.1, 67.3 **(Figure A.35, Appendix A)**. IR (ATR, cm^{-1}): 3455 (broad, O-H st), 1664 (C=O st) **(Figure A.36, Appendix A)** [48].

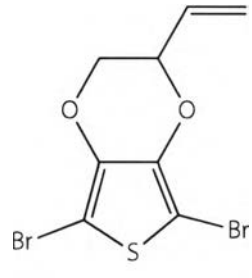
2.3.11 2-Vinyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine 6

6

Compound **5k** (0.256 g, 1.00 mmol), cuprous oxide (0.042 g, 0.30 mmol), quinoline (0.35 mL, 3.00 mmol), 10 mL of dimethylsulfoxide were mixed and allowed

to stir for 5 h at reflux under nitrogen atmosphere. The mixture was then cooled to room temperature and filtered. The filtrate was added ethyl acetate (10 mL) and washed with 10% hydrochloric acid three times. The organic layer was dried over anhydrous magnesium sulfate, filtered and distilled under reduced pressure. The product was purified by column chromatography using hexane/dichloromethane (4 : 1) as eluent, affording pale yellow oil (0.100 g, 59.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.35 (s, 1H), 6.33 (s, 1H), 5.88 (m, 1H), 5.54 (d, *J* = 17.3 Hz, 1H), 5.40 (d, *J* = 10.7 Hz, 1H), 4.63 (m, 1H), 4.20 (m, 1H), 3.90 (m, 1H) **(Figure A.37, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 141.7, 141.4, 131.9, 119.5, 99.7, 99.5, 74.1, 67.9 **(Figure A.38, Appendix A)**. IR (ATR, cm^{-1}): 2915 (-CH st), 1478 (C=C st), 1179 (C-O st) **(Figure A.39, Appendix A)** [48].

2.3.12 5,7-Dibromo-2-vinyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine 7

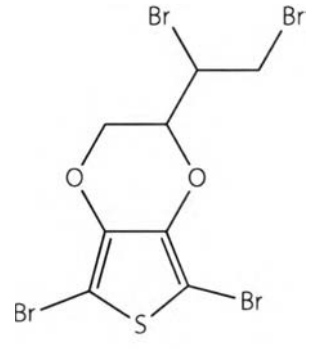


7

Compound **6** (0.027 g, 0.16 mmol) and *N*-bromosuccinimide (0.071 g, 0.40 mmol) in dichloromethane (5 mL) were mixed and allowed to stir for 5 min at room temperature. The reaction mixture was quenched with saturated sodium hydrogen carbonate solution and washed with 2 M sodium hydroxide. The reaction mixture was dried over anhydrous magnesium sulfate, filtered and distilled under reduced pressure to give the product as pale yellow liquid (0.050 g, 96.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.93 – 5.82 (m, 1H), 5.55 (d, *J* = 17.4 Hz, 1H), 5.44 (d, *J* = 10.7 Hz, 1H), 4.67 (s, 1H), 4.26 (d, *J* = 12.2 Hz, 1H), 4.00 – 3.92 (m, 1H) **(Figure A.40, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.6, 139.4, 130.7, 120.4, 85.5, 85.4, 74.6, 68.1 **(Figure A.41,**

Appendix A). IR (ATR, cm^{-1}): 2913 (-CH st), 1499, 1406, 1305 (C=C st), 1060 (C-O st) **(Figure A.42, Appendix A)** [49].

2.3.13 5,7-Dibromo-2-(1,2-dibromoethyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine 8

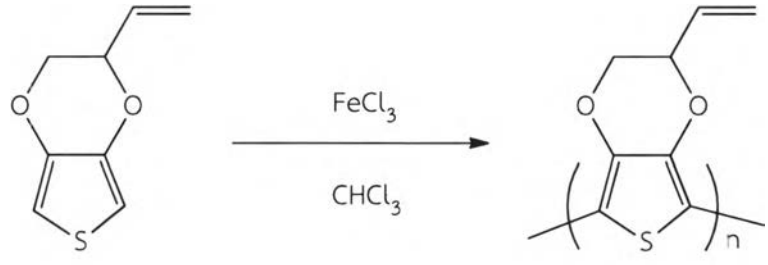


8

Compound **6** (0.119 g, 0.70 mmol) dissolved in dichloromethane (8 mL), pyridinium tribromind (1.119 g, 3.50 mmol) and pyridine (0.40 mL, 4.90 mmol) were mixed and allowed to stir for 4 h at room temperature under ambient atmosphere. The reaction mixture was quenched with 1 M sodium sulfite and washed with 10% HCl, water and saturated sodium chloride. The product was purified by column chromatography using hexane/toluene (9 : 1) as eluent, affording a colorless oil (0.059 g, 17.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.55 (dt, *J* = 8.7, 3.7 Hz, 1H), 4.45 (d, *J* = 3.7 Hz, 2H), 4.31 (dt, *J* = 9.0, 4.6 Hz, 1H), 4.01 (dd, *J* = 11.5, 4.7 Hz, 1H), 3.85 (dd, *J* = 11.5, 4.5 Hz, 1H). **(Figure A.43, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.2, 138.0, 86.4, 86.3, 74.3, 66.1, 47.0, 34.1. **(Figure A.44, Appendix A)**. IR (ATR, cm^{-1}): 2927 (-CH st), 1506, 1414 (C=C st), 1078 (C-O st) **(Figure A.46, Appendix A)**. and a white powder (0.080 g, 23.7%). mp. 154 °C (dec.) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.60 (dt, *J* = 8.5, 2.3 Hz, 1H), 4.35 – 4.21 (m, 3H), 4.09 (m, 1H), 3.84 (dd, *J* = 10.3, 4.7 Hz, 1H). **(Figure A.47, Appendix A)**. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 139.4, 139.2, 86.3, 85.9, 71.5, 68.6, 47.1, 30.7 **(Figure A.48, Appendix A).** IR (ATR, cm^{-1}): 2941 (-CH st), 1502, 1414 (C=C st), 1091 (C-O st) **(Figure A.50, Appendix A)**.

2.4 Polymer synthesis

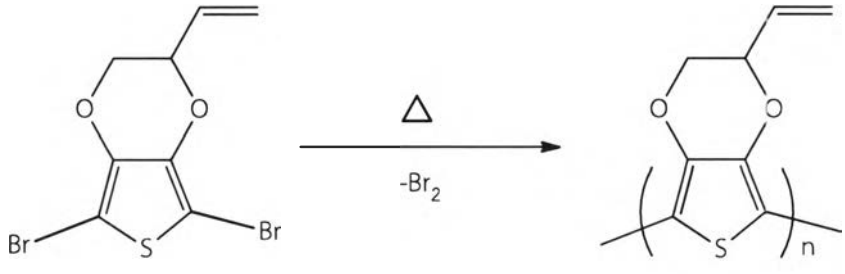
2.4.1 Oxidative polymerization of 2-vinyl-2,3-dihydrothieno[3,4-b][1,4] dioxine 6



6 9

A solution of compound **6** (0.084 g, 0.50 mmol) in chloroform (10 mL) was added dropwise to the solution of anhydrous Iron (III) chloride ($FeCl_3$) (0.243 g, 1.50 mmol) in chloroform (10 mL). The reaction mixture was allowed to stir for 6 days at room temperature under nitrogen atmosphere. The mixture was then added methanol (20 mL) to give dark black suspension which was stirred for another 2 h at room temperature. The black solid was filtered, washed with methanol and further purified by Soxhlet extraction for 2 days with methanol to give the corresponding polythiophene derivative as dark blue solid. (0.060 g, 72.2%). The polymer could not be dissolved in all common solvents. IR (ATR, cm^{-1}): 1485 (-CH st), 1275, 1114 (-CH bending) **(Figure A.51, Appendix A)**. λ_{max} = 552 nm [27].

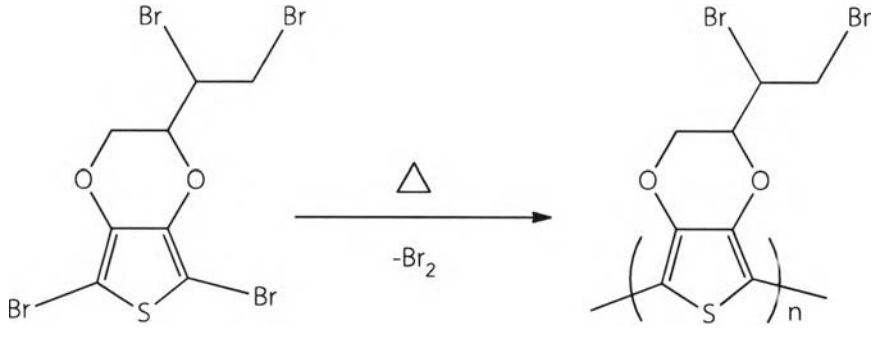
2.4.2 Thermal polymerization of 5,7-Dibromo-2-vinyl-2,3-dihydrothieno [3,4-*b*][1,4]dioxine 7



7 **9**

Compound **7** (0.194 g, 0.60 mmol) was placed in a round bottle flask. The compound **7** was heated at 70 °C for 105 days. During the process, the pale yellow liquid of compound **7** turned the dark blue solid state with slight appearance of brown bromine vapor. After completion of the reaction, the resulting dark blue solid was allowed to cool to room temperature and then washed with methanol to give the polythiophene **9** (0.068 g, 68.4%). The polythiophene was insoluble in all organic solvents. IR (ATR, cm^{-1}): 2924 (-CH st), 1686 (C=C st), 1321 (C-O st) **(Figure A.52, Appendix A).** λ_{max} = 668 nm [35].

2.4.3 Solid state polymerization of 5,7-Dibromo-2-(1,2-dibromoethyl)-2,3dihydrothieno[3,4-*b*][1,4]dioxine 8



8 **10**

Compound **8** (0.054 g, 0.11 mmol) was placed in a round bottle flask. The flask was heated at 120 °C for 3 days, during period the white solid turned dark blue with slight appearance of brown bromine vapor. After completion of the reaction, the resulting dark blue solid was allowed to cool to room temperature and then washed with dichloromethane to give the polythiophene derivative as dark blue solid. (0.018 g, 45.4%). The polymer could not be dissolved in all common solvents. IR (ATR, cm^{-1}): 1490 (-CH st), 1281, 1183 (-CH bending) **(Figure A.53, Appendix A)**. λ_{max} = 688 nm [35].